Observation of All-Metal Aromatic Molecules
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Aromaticity is a concept invented to account for the unusual stability of an important class of organic molecules: the aromatic compounds. Here we report experimental and theoretical evidence of aromaticity in all-metal systems. A series of bimetallic clusters with chemical composition \( \text{MAL}_n^- \) (\( M = \text{Li}, \text{Na}, \text{or Cu} \)), was studied and compared with photoelectron spectroscopy and ab initio calculations. All the \( \text{MAL}_n^- \) species possess a pyramid structure containing an \( M^- \) cation interacting with a square \( \text{Al}_4^{2-} \) unit. Ab initio studies indicate that \( \text{Al}_4^{2-} \) exhibits aromaticity with two delocalized \( \pi \) electrons (thus following the 4n + 2 electron counting rule) and a square planar structure and maintains its structural and electronic features in all the \( \text{MAL}_n^- \) complexes. These findings expand the aromaticity concept into the arena of all-metal species.

The name “aromatic compound” was initially bestowed on benzene, its derivatives, and related compounds because of their aroma. Today, the terms “aromatic” and “aromaticity” are used to describe cyclic, planar, and conjugated molecules possessing \( (4n + 2) \) \( \pi \) electrons and having specific chemical and structural stability. Despite the undeniable usefulness of the aromaticity concept, it remains controversial and its physical origin is still being debated (1–3). Thus, recent years have seen a resurgence in the development of various criteria of aromaticity and in theoretical investigations aimed at gaining a deeper insight into the origin of this phenomenon (4–9). In this report, we present experimental and theoretical evidence of aromaticity in an all-metal system: the \( \text{Al}_4^{1-} \) dianion in a series of bimetallic ionic systems with chemical composition \( \text{MAL}_n^- \) (\( M = \text{Li}, \text{Na}, \text{or Cu} \)). The \( \text{Al}_4^{2-} \) unit was found to be square planar and to possess two delocalized \( \pi \) electrons, thus conforming to the \((4n + 2)\) electron counting rule for aromaticity.

Using a laser vaporization source and negative ion photoelectron spectroscopy (9, 10), we produced and investigated a series of \( \text{MAL}_n^- \) clusters (11). The negative ion technique affords convenient size selectivity, and photoelectron spectroscopy is quite suitable for providing unique electronic structure information pertaining to the neutral species. We have found that combining photoelectron spectroscopy and ab initio calculations offers a particularly powerful approach to investigating the structure and bonding of novel molecular and cluster species (12). Photoelectron spectra of the three \( \text{MAL}_n^- \) species were measured at two different photon energies. The spectra of the three species are similar (Fig. 1), each with an intense threshold peak (\( \chi \) and \( A \)) followed by two weaker features (\( B \) and \( C \)). The \( X \) and \( A \) features overlapped heavily and were only resolved in the 355-nm spectrum of \( \text{NaAl}_4^- \). The vertical electron detachment energies of these features were measured from the peak maxima (Table 1) and compared to the results of the...
Fig. 1. Photoelectron spectra at 355 nm (3.496 eV) for (A) LiAl$_4^-$, (B) NaAl$_4^-$, and (C) CuAl$_4^-$ and at 266 nm (4.661 eV) for (D) LiAl$_4^-$, (E) NaAl$_4^-$, and (F) CuAl$_4^-$.

The highest occupied molecular orbital (HOMO), which is doubly occupied, is a delocalized π orbital; the rest of the molecular orbitals are either bonding σ-type or lone pairs. The observation of the delocalized π HOMO is surprising. We found that a similar delocalized π orbital is also present in the MAI$_4^-$ species in both its pyramidal and planar isomers. This π orbital holds the key to understanding the structure and bonding of the MAI$_4^-$ species.

Examination of its structure and bonding revealed that Al$_4^{2-}$ exhibits characteristics of aromaticity. First, it possesses two completely delocalized π electrons (Fig. 3), which satisfy the $(4n + 2)$ electron counting rule for aromatic compounds. Second, Al$_4^{2-}$ has a perfect square structure, due to the delocalization of the π electrons, exactly as expected for an aromatic system. Analogy can be made with the prototypical aromatic system, benzene, in which aromaticity is responsible for its perfect hexagonal structure with all equal C-C bonds, rather than the classical alternating single and double bonds. Finally, like benzene in M(C$_6$H$_6$)$_2$ sandwich complexes, the Al$_4^{2-}$ dianion preserves its structural integrity in forming the MAI$_4^-$ complexes (Fig. 2). Furthermore, we found that the vibrational frequencies of the isolated Al$_4^{2-}$ dianion are very similar to those in the pyramidal and planar structures of the three MAI$_4^-$ species. We also investigated theoretically the structures of neutral M$_2$Al$_4$ species and found
again that the most stable structures contain the intact Al$_2^{2-}$ dianion.

Polyanions of the main group elements (known as Zintl anions) are building blocks of an interesting class of ionic solids (13, 16). Zintl phases with the stoichiometry Na$_2$In, Na$_2$K$_2$Tl$_2$O$_3$, Li$_3$In$_2$, and many others [see a recent review (15)] have been synthesized, in which cationation (element element bonding) leads to the formation of In$_4^{8-}$, Tl$_4^{10-}$, and In$_5^{9-}$ multiply charged cluster anions. However, despite the fact that a large number of Ga, In, and TI Zintl anions have been synthesized, their AI analogs are still elusive (15). The current Al$_4^{2-}$ dianion is fundamentally different from the previously discovered heavy group-13 X$_3^{2-}$-type polyanions, which are all tetrahedral. We believe that aromatic square planar Al$_4^{2-}$ clusters, like Al$_2^{2-}$, may in fact exist for the heavier group-13 elements (Ga, In, and TI). Therefore, the current finding may not only expand the aromaticity concept into an all-metal system but may also indicate whole classes of new inorganic aromatic species.

### References and Notes


11. The MAI$_n^{-}$ species were produced with a laser vaporization supersonic cluster source. A Cu/Al alloy target was used to produce the CuAl$_n$ anions, whereas an AlU$_3$CO$_3$ (Na$_2$CO$_3$) composite target was used to produce LiAl$_n$ (NaAl$_n$). The anionic species produced were analyzed with a time-of-flight mass spectrometer. The MAI$_n^{-}$ anions of interest were selected for photodetachment in each experiment. Photoelectron spectra were taken at two detachment laser wavelengths, 355 and 266 nm, and were calibrated using the known spectra of Cu$^+$. The photoelectron energy resolution was about 25 meV for 1-eV electrons.


13. We initially optimized geometries and calculated frequencies of Cu$_2$[Al$_2^{2-}$], Na$_2$[Al$_2^{2-}$], Li$_2$[Al$_2^{2-}$], and [Al$_2^{2-}$] using analytical gradients with polarized split-valence basis sets (6-311+G*) and a hybrid method known in the literature as B3LYP. Then we refined geometries and calculated frequencies at the second-order Møller-Plesset perturbation theory (MP2) level. Na$_2$[Al$_2^{2-}$], Li$_2$[Al$_2^{2-}$], and [Al$_2^{2-}$] were further studied using the coupled-cluster method [CCSD(T)] with the 6-311+G* basis sets. The energies of the most stable structures were refined using the CCSD(T) method and the more extended 6-311+G(2df) basis sets. The vertical electron detachment energies were calculated using the outer valence Green Function method [OVGF/6-311+G(2df)] and the MP2/6-311+G* geometries for Cu$_2$[Al$_2^{2-}$] and the CCSD(T)/6-311+G* geometries for Li$_2$[Al$_2^{2-}$] and Na$_2$[Al$_2^{2-}$]. Core electrons were kept frozen in treating the electron correlations at the MP2, CCSD(T), and OVGF levels of theory. All calculations were performed using the Gaussian 98 program.

14. The Gaussian 98 program (revision A.7) is by M. J. Frisch et al. (Gaussian, Inc., Pittsburgh, PA, 1998).


17. Molecular orbital pictures were made using the MOLDEN3.4 program (G. Schaftenaar, MOLDEN3.4, Computer Assisted Organic Synthesis/Computer Assisted Molecular Modeling Center, The Netherlands (1998)).

18. The theoretical work done at Utah State University is supported by the donors to The Petroleum Research Fund, administered by the American Chemical Society. The experimental work done at Washington State University is supported by NSF. The experiment was performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's (DOE's) Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle. L.S.W. is an Alfred P. Sloan Foundation Research Fellow.

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**Table 1.** Experimental (exp.) and theoretical (theo.) vertical electron detachment energies in eV for LiAl$_4^{2-}$, NaAl$_4^{2-}$, and CuAl$_4^{2-}$. MO, molecular orbital.

<table>
<thead>
<tr>
<th>Observed features</th>
<th>VDE (exp.)</th>
<th>Square pyramid</th>
<th>Fully planar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MO</td>
<td>VDE (theo.)*</td>
<td>MO</td>
</tr>
<tr>
<td>X</td>
<td>2.15 ± 0.06</td>
<td>3a$_1$</td>
<td>4a$_1$</td>
</tr>
<tr>
<td>A</td>
<td>2.20 ± 0.06</td>
<td>1b$_1$</td>
<td>1b$_1$</td>
</tr>
<tr>
<td>B</td>
<td>2.82 ± 0.08</td>
<td>2a$_1$</td>
<td>3a$_1$</td>
</tr>
<tr>
<td>C</td>
<td>3.09 ± 0.04</td>
<td>1b$_2$</td>
<td>2b$_2$</td>
</tr>
</tbody>
</table>

| NaAl$_4^{2-}$      | X          | 2.04 ± 0.05   | 3a$_1$       | 1.92 (0.86)  |
|                   | A          | 2.09 ± 0.05   | 1b$_1$       | 2.05 (0.85)  |
|                   | B          | 2.70 ± 0.05   | 2a$_1$       | 2.52 (0.86)  |
|                   | C          | 2.96 ± 0.05   | 1b$_2$       | 2.86 (0.84)  |

| CuAl$_4^{2-}$      | X          | 2.32 ± 0.06   | 2b$_1$       | 2.32 (0.86)  |
|                   | A          | 2.35 ± 0.06   | 4a$_1$       | 2.39 (0.87)  |
|                   | B          | 3.24 ± 0.09   | 2b$_2$       | 3.35 (0.85)  |
|                   | C          | 3.84 ± 0.06   | 3a$_1$       | 3.65 (0.86)  |

*The VDEs were calculated at the OVGF/6-311+G(2df) level of theory. The numbers in parentheses indicate the pole strength, which characterizes the validity of the one-electron detachment picture.